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(54) HIGH-OIL-ABSORPTIVE POROUS SILICA, PRODUCTION THEREOF AND CARRIER

(57)Abstract:

PURPOSE: To improve oil absorptivity by drying a silica hydrogel obtained by the reaction of an alkali metal silicate having SiO2 of a specific conc. or below with a mineral acid at the critical temp. or above of a solution.

CONSTITUTION: A mineral acid such as sulfuric acid is added into an aq. alkali metal silicate solution such as Na2SiO3 adjusted to ≥60g/l SiO2 conc. by diluting with water at a prescribed temp. A SiO2 slurry produced by aging at the temp., raising the temp. and furthermore adding the mineral acid is adjusted in pH, is filtered, washed and suspended again in water. By-product Na2SO4 is removed by refilteration and washing to obtain a hydrogel. By suspending the hydrogel in a solvent such as methanol, filtering and cleaning, a silica methanogel is obtained. The silica methanogel is suspended in a solvent such as methanol, is heated up to the critical point of the solvent (Tc=240°C, Pc=78.7atm) and is cooled to obtain the high-oil-absorptive porous SiO2 having ≥350ml/100g oil absorption and ≥5ml/g narrow pore volume by the mercury porosimeter.

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CLAIMS

[Claim(s)]
[Claim 1] The high oil absorption nature porosity silica whose pore volume according [the oil absorption by JIS-K-5101 law] to 350ml / 100g or more, and the mercury porosimeter is 5ml/g or more.
[Claim 2] The manufacture approach of the silica according to claim 1 characterized by drying the silica hydrogel from which SiO2 concentration was obtained by the reaction of the alkali-metal silicate of 60 or less g/l, and a mineral acid above the critical point of the solvent.
[Claim 3] Support which consists of a silica according to claim 1.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to support, such as physic and agricultural chemicals, at the porosity silica which has high oil absorption nature, and its manufacture approach list.

[0002]
[Description of the Prior Art] Conventionally, pore volume is large, and the reaction condition of sodium silicate and a sulfuric acid is controlled as an approach of obtaining a silica with high oil absorption capacity, for example, or the approach of drying the generated silica hydrogel, hydrothermal processing and after carrying out acid treatment is learned (JP,58-135119,A).

[0003] However, the pore volume by the mercury porosimeter of the conventional silica was 4.5 ml/g extent at the maximum, and the oil absorption by JIS-K-5101 law was a thing (300ml / 100g or less).

[0004] Although the silica is conventionally used widely as support, such as physic and agricultural chemicals, a disintegration agent, various adsorbents, etc., in the application of such a silica, what gives the fluidity which was excellent even when it had high oil absorption nature further and adsorption maintenance of the various oily matter etc. was carried out so much rather than the silica obtained with the conventional technique is desired.

[0005]
[Means for Solving the Problem and its Function] In order that this invention persons may meet the above-mentioned request, as a result of inquiring wholeheartedly, the silica hydrogel which SiO2 concentration becomes from the floc of a detailed primary particle by the reaction of the comparatively low-concentration alkali-metal silicate of 60 or less g/l and a mineral acid is manufactured, By carrying out supercritical drying of this silica hydrogel above the critical point of that solvent The oil absorption by JIS-K-5101 law is 350ml / 100g or more. Compared with the conventional silica (white carbon) whose pore volume by the mercury porosimeter is 5ml/g or more, it has big oil absorption capacity in each stage, and the knowledge of the new, very large porosity silica (silica aerogel) of pore volume being obtained was carried out. This porosity silica has the outstanding fluidity, when adsorption maintenance of the oily matter, such as n-butyl phthalate, is carried out so much. For this reason, furthermore, as support, such as physic and agricultural chemicals, and a disintegration agent Moreover, it is useful as various adsorbents, the knowledge of the ability to use it suitably also to the application of a heat insulator, sound insulation, a thickener, a thixotropy grant agent, the various bulking agents for functional papers (a diazo type paper, ink jet paper, etc.), etc. further is carried out, and it comes to make this invention.

[0006] In addition, conventionally, the so-called sol-gel method is adopted and carrying out supercritical drying of the silica produced by hydrolysis and gelation of alkoxysilane is known. However, the porosity silica with large oil absorption called 5 or more ml/g of pore volume by oil absorption of 350ml which was mentioned above depending on such an approach / 100g or more, and the mercury porosimeter, and pore volume is not obtained. Unless it is not obtained for the first time and a porous silica hydrogel is obtained in the phase of a reaction in this case by carrying out supercritical drying of the silica hydrogel of the porosity acquired when the porosity silica with large oil absorption of this invention and pore volume makes a low-concentration alkali-metal silicate react with a mineral acid, even if it carries out supercritical drying, the porosity silica with large above oil absorption and pore volume is not obtained. Moreover, even if a porous silica hydrogel is obtained in the phase of a reaction, and it adopts the usual desiccation approach and dries this, similarly the porosity silica (silica aerogel) of this invention is not obtained.

[0007] Hereafter, lessons is taken from this invention and it explains in more detail.

[0008] It is 400ml / 100g or more more preferably, and 350ml / 5 or more ml/g of pore volume by the mercury porosimeter have [the oil absorption according / the porosity silica (silica aerogel) of this invention / to JIS-K-5101 law] more preferably 5.5 or more ml/g 100g or more. Moreover, transparency is size and the silica of this invention has high **.

[0009] moreover, a specific surface area (nitrogen adsorption process) the pore volume usually according [this porosity silica] to nitrogen adsorption hasg 1.5ml [/] or more in 2ml /or more more preferablyg, and according to a BET adsorption method -- 200-700m2/g -- it has 400-600m2/g more preferably.

[0010] While the porosity silica of this invention is the floc of a primary particle and the primary particle diameter of the average is usually 5-100nm, the average diameter of floc is 1-50 micrometers.

[0011] More preferably, SiO2 concentration can manufacture a silica hydrogel by the reaction of the alkali-metal silicate of 40 or less g/l, and mineral acids, such as a sulfuric acid, and can obtain 60 or less g/l of silicas of this invention by drying this silica hydrogel above the critical point of that solvent.

[0012] In this case, if concentration of an alkali-metal silicate is made high on the occasion of manufacture of a silica hydrogel, the porosity silica of this invention will not be obtained. Moreover, although the reaction of an alkali-metal silicate and a mineral acid can be performed according to a well-known approach, if reaction temperature is too high, the case where a detailed silica hydrogel is not obtained will arise.

[0013] Although supercritical drying of a silica hydrogel is performed by drying above the critical point of the solvent and it can carry out according to a supercritical drying method well-known as the approach The silica hydrogel obtained at the above-mentioned reaction as it is in this case, in order to make it make it dry above the critical point (Tc=374.2 degree C, Pc=218atm) of water while water had been included or to lower a critical condition, [namely,] After permuting the water in a silica hydrogel by other solvents (for example, organic solvents, carbon dioxides, etc., such as alcohol), it may be made to carry out supercritical drying of this.

[0014] The porosity silica of this invention has large pore volume, as mentioned above, oil absorption is high, and the fluidity which was excellent where adsorption maintenance of a lot of oily matter etc. is carried out is shown. For this reason, the engine performance which was very excellent as support, such as physic and agricultural chemicals, and a disintegration agent is given, and it is effectively used also as various adsorbents. Furthermore, it is used using such description suitable for the application of applications, such as an application of a heat insulator, sound insulation, etc., a thickener, and a thixotropy grant agent, the various bulking agents for functional papers, etc.

[0015]
[Example] Although an example and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example.

[0016] 142ml of sulfuric acids of concentration 560 g/l was added keeping 5l. of solutions which diluted the No. 3 sodium silicate (SiO2/Na2O=3.2) of [example 1] marketing with water, and prepared SiO2 concentration to 38 g/l at 60 degrees C. Subsequently, after riping for 30 minutes at this temperature, the temperature up was carried out to 90 degrees C, and 17ml of sulfuric acids of this concentration was added further.

[0017] After adjusting and rinsing [filtered and] pH of the obtained silica slurry to 5, it re-suspended in water. Furthermore, pH was adjusted to 4, filtration and rinsing were performed again, the sodium sulfate of a by-product was removed, and the silica hydrogel was obtained.

[0018] It filtered and swabbed in methanol, after suspending this silica hydrogel 1kg (90% of water content) in 1l. of methanols. Furthermore, the obtained silica cake was again suspended in 1l. of methanols, filtration and methanol swabbing were performed, and silica methano gel was obtained.

[0019] It cooled and silica aerogel was obtained, after lowering a pressure to atmospheric pressure gradually, having heated the autoclave until it put into the autoclave, it sealed and it became the critical point (Tc=240 degree C, Pc=78.7atm) of a methanol, and keeping temperature at 240 degrees C or more then, after suspending this silica methano gel in 1l. of methanols.

[0020] The apparent specific gravity of this silica aerogel was 0.10 ml/g, and grain size was 50= 15.52 micrometers of D, 80= 30.51 micrometers of D, and 97= 49.55 micrometers of D.

[0021] Hot air drying of the silica hydrogel obtained in the [example 1 of comparison] example 1 was carried out at 140 degrees C for 1 hour, and silica xerogel was obtained.

[0022] 148ml of sulfuric acids of concentration 560 g/l was added keeping 5l. of solutions which diluted the No. 3 sodium silicate (SiO2/Na2O=3.2) of the [example 2 of comparison] marketing with water, and prepared SiO2 concentration to 76 g/l at 90 degrees C. Subsequently, after riping for 30 minutes at this temperature, 167ml of sulfuric acids of this concentration was added further.

[0023] After adjusting and rinsing [filtered and] pH of the obtained silica slurry to 5, it re-suspended in water. Furthermore, pH was adjusted to 4, filtration and rinsing were performed again, the sodium sulfate of a by-product was removed, and the silica hydrogel was obtained.

[0024] It filtered and swabbed in methanol, after suspending this silica hydrogel 1kg (90% of water content) in 1l. of methanols. Furthermore, the obtained silica cake was again suspended in 1l. of methanols, filtration and methanol swabbing were performed, and silica methano gel was obtained.

[0025] After suspending this silica methano gel in 1l. of methanols, supercritical drying was performed like the example 1 and silica aerogel was obtained.

[0026] Next, the description (the pore volume by the mercury porosimeter, the specific surface area by the BET adsorption method, the pore volume by nitrogen adsorption, the diameter of a pore peak, oil absorption by JIS-K -5101) of the silica of an example 1 and the examples 1 and 2 of a comparison was measured. A result is shown in Table 1. In addition, the description of a commercial wet silica was written together in Table 1.

[0027]
[Table 1]

物性値	実施例1	比較例1	比較例2	市販品A	市販品B	市販品C	市販品D
Vp (Hg)	5.56	1.17	5.16	4.44	4.26	3.70	4.29
SN_2	430	500	135	298	160	203	200
Vp (N_2)	2.31	0.62	0.71	1.70	1.50	0.73	0.70
D peak	18.6	6.2	2nm以下	22.8	41.6	—	—
O. A.	451	115	231	289	256	233	238

**** (Hg) : Pore volume by the mercury porosimeter (ml/g)
SN2 : Specific surface area by the BET adsorption method (m2/g)
**** (N2) : Pore volume by nitrogen adsorption (ml/g)
D peak : Diameter of a pore peak (nm)
O.A. : Oil absorption by JIS-K -5101 (ml / 100g)

[0028] The porosity silica (silica aerogel) of the example manufactured by carrying out supercritical drying of the

silica hydrogel obtained at the reaction of a comparatively low-concentration alkali-metal silicate and a sulfuric acid from the result of Table 1 has very big pore volume compared with a commercial wet silica, and it is admitted that oil absorption capacity is also high. Since the porosity silica (silica aerogel) was obtained with the opening structure of this detailed silica hydrogel held, this was considered while the detailed silica hydrogel was obtained at the above-mentioned reaction.

[0029] On the other hand, although it is thought by the usual desiccation approach that it is because contraction of the silica particle by the surface tension of water takes place in the process of desiccation and pore is destroyed even if a detailed silica hydrogel is obtained at a reaction so that the example 1 of a comparison may show When the silica hydrogel which has detailed structure at a reaction was not generated even if it used supercritical drying so that pore volume might be small, and only precise silica gel with small oil absorption might be obtained and the example 2 of a comparison might show, it was that from which the silica gel of high oil absorption nature is not obtained similarly.

[0030] Next, although 300ml (66.7 v/w%) addition of the 0ml (DBP) (0 v/w%) of the 150ml (50 v/w%) of the n-butyl phthalate was carried out at these silicas 150g and it mixed with the desk kneader (inlet company, PNV-2H) for 15 to 25 minutes about the fluidity of the porosity silica of the above-mentioned example 1, and a commercial wet silica, it evaluated by measuring condensation and a fluidity index. A result is shown in drawing 1 -2. In addition, A-D in drawing is as a result of commercial wet silica A-D, respectively.

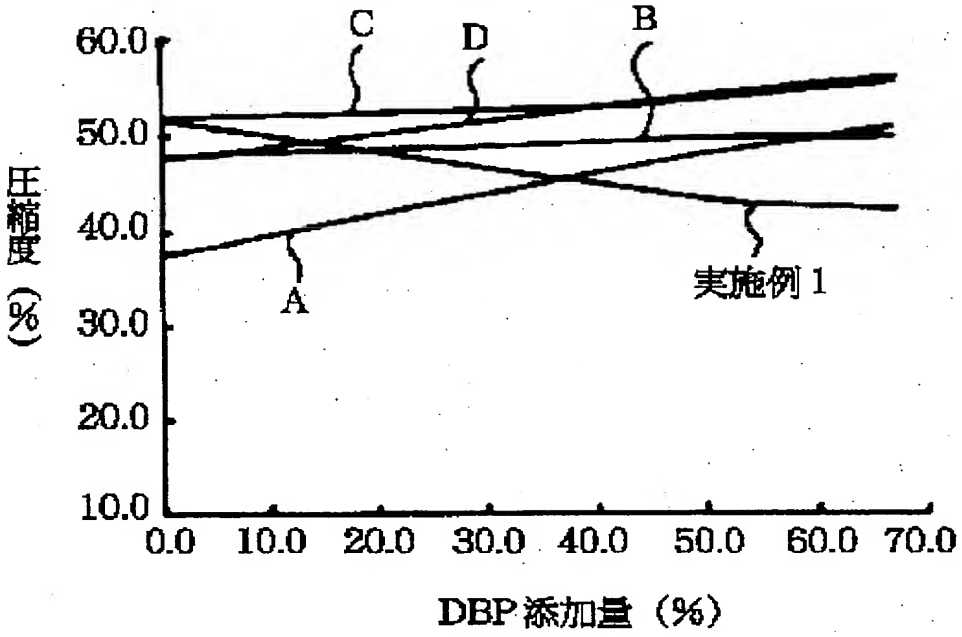
[0031] Drawing 1 shows the relation between a DBP addition and condensation. Condensation is the most closely related factor at the flowability of fine particles, and hardens with looseness apparent-specific-gravity X, and it is calculated by the formula of apparent-specific-gravity Y to 100- (Y-X) / X, and a fluidity worsens, so that the value is large. Moreover, having the fluidity which was very [than the conventional silica] excellent in the condition of the silica of an example 1 containing DBP so much from the result of drawing 1 and 2, and adsorbing although a fluidity becomes good so that drawing 2 shows the relation between a DBP addition and a fluidity index, a fluidity index (NF) has the relation of condensation (C) and NF=100-1.35C and this value is large is admitted. Therefore, the knowledge of the silica of this invention having very high usefulness as support, such as agricultural chemicals, etc. is carried out from this.

[0032]
[Effect of the Invention] Compared with the conventional wet method silica, it has very big pore volume, and the oil absorption capacity of the porous silica of this invention is also high, and it shows the fluidity excellent in the condition of adsorbing oily matter so much and holding, and is used suitable for support, such as physic and agricultural chemicals, and others.

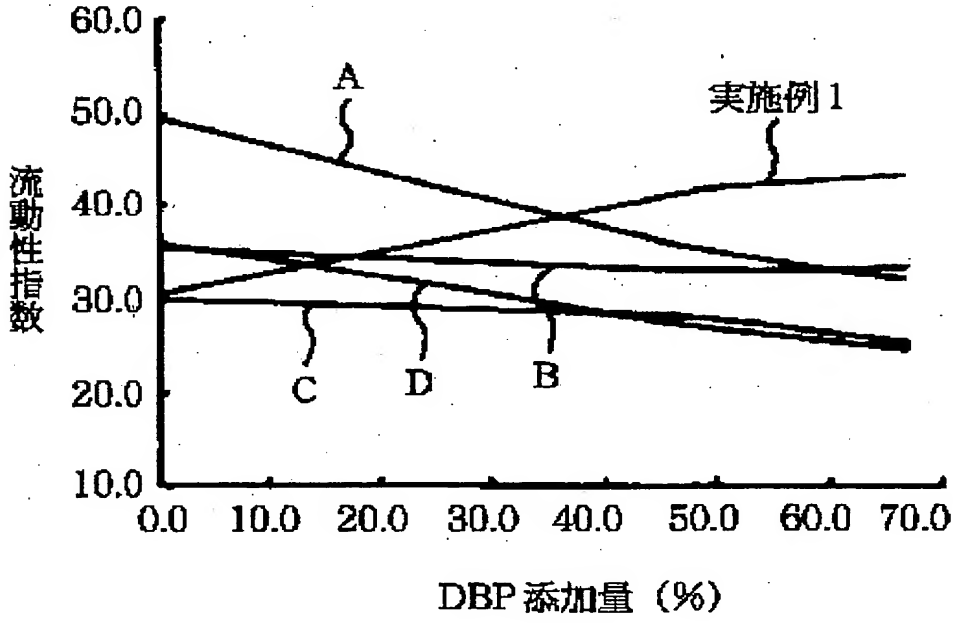
[0033] Moreover, according to the manufacturing method of this invention, this porous silica can be manufactured certainly and easily.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the graph which shows the condensation at the time of carrying out adsorption maintenance of the DBP to various silicas.
[Drawing 2] It is the graph which shows the fluidity index at the time of carrying out adsorption maintenance of the DBP to various silicas.



Drawing 2



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[Method of Amendment] Modification
[Proposed Amendment]

[0005]
[Means for Solving the Problem and its Function] For this invention persons, in order to meet the above-mentioned request, as a result of inquiring wholeheartedly, SiO2 concentration is the reaction of the comparatively low-concentration alkali-metal silicate of 60 or less g/l, and a mineral acid. Manufacturing the silica hydrogel which consists of floc of a detailed primary particle, and by carrying out supercritical drying of this silica hydrogel above the critical point of that solvent, the oil absorption by JIS-K-5101 law was 350ml / 100g or more, compared with the conventional silica (white carbon) whose pore volume by the mercury porosimeter is 5 or more ml/g, it is markedly alike, and has big oil absorption capacity, and the knowledge of the new, very large porosity silica (silica aerogel) of pore volume being obtained was carried out. Furthermore, this porosity silica has the fluidity which was excellent when adsorption maintenance of the oily matter, such as n-butyl phthalate, was carried out so much, and, for this reason, is support, such as physic and agricultural chemicals, and a disintegration agent, Moreover, it is useful as various adsorbents, the knowledge of the ability to use it suitably also to the application of a heat insulator, sound insulation, a thickener, a thixotropy grant agent, the various bulking agents for functional papers (a diazo type paper, ink jet paper, etc.), etc. further is carried out, and it comes to make this invention.